FLOQUET–LIOUVILLE SUPER-MATRIX APPROACH FOR MULTIPHOTON NON-LINEAR OPTICAL PROCESSES IN INTENSE LASER FIELDS

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A practical non-perturbative approach is presented for the treatment of multiphoton non-linear optical processes in intense monochromatic or polychromatic field. By extending the many-mode Floquet theory recently developed by the authors, the time-dependent Liouville equation for the density matrix of atoms or molecules undergoing radiative and/or collisional relaxations can be transformed into an equivalent *time-independent* Floquet–Liouville super-matrix eigenvalue problem. The method is illustrated by a study of the *multiphoton* resonance fluorescence spectra of two-level systems.

The study of non-linear optical processes such as multiphoton dissociation of molecules, resonance fluorescence, Raman scattering, and wave mixings, etc. is a subject of much current interest [1,2] both theoretically and experimentally. At lower fields, perturbative and diagrammatic methods [2] are often used for non-resonant phenomena, whereas the rotating wave approximation (RWA) is most commonly adopted for near resonant processes [2,3]. The semiclassical Floquet approaches based on the Schrödinger equation, while providing non-perturbative means for the studies of multiphoton ionization, excitation, and dissociation processes at high fields [4], cannot be applied to processes undergoing relaxations due to radiative decays and collision dampings, etc. In this Letter we advance a general non-perturbative semiclassical treatment of the Liouville equation (allowing for relaxation mechanisms) for the density matrix operator of atomic or molecular systems exposed to intense monochromatic or polychromatic fields. By extending the many-mode Floquet theory (MMFT) recently developed [5], the time-dependent Liouville equation can be transformed into an equivalent time-independent Floquet–Liouville super-matrix (FLSM) eigenproblem. In addition to being numerically stable and computationally efficient, the FLSM method is capable of treating non-resonant and resonant, one-photon and multiphoton, steady-state and transient phenomena on an equal footing.

The Liouville equation for the time evolution of a set of N-level quantum systems, interacting with several coherent linearly polarized monochromatic fields, undergoing relaxation by Markovian processes is ($\hbar = 1$)

$$\mathrm{i}\partial_t \hat{\rho}(t) = [\hat{H}(t), \hat{\rho}(t)] + \mathrm{i}[\hat{R}\,\hat{\rho}(t)]. \tag{1}$$

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Here $\hat{\rho}$ is the density matrix of the system, reduced by an averaging over all irrelevant degrees of freedom acting as a thermal bath, and $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$. $\hat{H}_0$ is the unperturbed atomic Hamiltonian with eigenvalues $\{E_\alpha\}$ and eigenvectors $\{|\alpha\rangle\}$, $\alpha = 0,1,2,...,N-1$, and $V(t)$ is the interaction Hamiltonian between the system and the M-mode classical fields given by

$$\hat{V}(t) = -\sum_{i=1}^{M} \boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}_i \cos(\omega_i t + \phi_i),$$

where $\boldsymbol{\mu}$ is the atomic dipole moment, $\boldsymbol{\varepsilon}_i$ the field amplitude, ω_i the frequency and μ_i the phase of the ith field. The relaxation term $[\hat{R}\,\hat{\rho}(t)]$ consists of T_1 (population damping) and T_2 (coherent damping) mechanisms which are due to the coupling of the atomic system to the thermal bath by radiative decays and collisions, etc. More explicitly [3]

$$(\hat{R}\,\hat{\rho})_{\alpha\alpha} = -\Gamma_{\alpha\alpha}\rho_{\alpha\alpha} + \sum_\beta \gamma_{\beta\alpha}\rho_{\beta\beta} \qquad (T_1), \tag{2}$$

$$(\hat{R}\,\hat{\rho})_{\alpha\beta} = -\Gamma_{\alpha\beta}\rho_{\alpha\beta} \quad (\alpha \neq \beta) \qquad (T_2), \tag{3}$$

where the phenomenological damping parameter $\Gamma_{\alpha\alpha}$ describes the population decay, $\Gamma_{\alpha\beta}$ the phase relaxation and $\gamma_{\beta\alpha}$ the feeding. In the following we shall confine our discussion to closed systems, namely, $\mathrm{Tr}[(\hat{R}\,\hat{\rho})] = 0$. Extension to open systems is straightforward.

In the tetradic or Liouville space [6] spanned by $|\alpha\rangle\langle\beta|$, where $\alpha,\beta = 0,1,...,N-1$, eq. (1) can be rewritten as $\mathrm{i}\partial_t\hat{\boldsymbol{\rho}}(t) = \hat{L}(t)\,\hat{\boldsymbol{\rho}}(t) + \mathrm{i}f$, or in matrix form,

$$\mathrm{i}\partial_t\rho_{\alpha\beta}(t) = \sum_{\mu\nu} \hat{L}_{\alpha\beta,\mu\nu}(t)\,\rho_{\mu\nu}(t) + \mathrm{i}f_{\alpha\beta}, \tag{4}$$

where $\hat{L}(t)$ is the superoperator or Liouvillian which is non-singular, whose matrix elements are, assuming $|0\rangle$ is the ground level,

$$\hat{L}_{00;\mu\nu}(t) = \hat{H}_{0\mu}(t)\,\delta_{0\nu} - \hat{H}_{\nu 0}(t)\,\delta_{0\mu} - \mathrm{i}(\Gamma_{00} + \gamma_0)\delta_{\mu 0}\delta_{\nu 0} - \mathrm{i}\left(\sum_\beta (1-\delta_{\beta\mu})\gamma_{\beta 0}\right)\delta_{\mu\nu}(1-\delta_{0\mu}), \tag{5}$$

$$\hat{L}_{\alpha\beta;\mu\nu}(t) = \hat{H}_{\alpha\mu}(t)\,\delta_{\beta\nu} - \hat{H}_{\nu\beta}(t)\,\delta_{\alpha\mu} - \mathrm{i}(\Gamma_{\mu\nu}\delta_{\alpha\mu}\delta_{\beta\nu} - \gamma_{\mu\beta}\delta_{\alpha\beta}\delta_{\mu\nu}) \qquad (\alpha \neq 0, \beta \neq 0), \tag{6}$$

and f is the source term, $f_{\mu\nu} = \gamma_0\delta_{\mu 0}\delta_{\nu 0}$ with $\gamma_0 = \Sigma_\beta\gamma_{\beta 0}$. The homogeneous solution of eq. (4) can be solved most expediently by invoking the many-mode Floquet theory [5] (MMFT), analogous to solving the Schrödinger equation with Hamiltonian having the same time dependence as that in eq. (1). The MMFT renders the time-dependent problem into an equivalent time-independent infinite-dimensional super-eigenvalue equation, namely,

$$\sum_{\sigma\tau}\sum_{\{k\}} \langle\alpha\beta;\{m\}|\hat{L}_\mathrm{F}|\sigma\tau;\{k\}\rangle\langle\sigma\tau;\{k\}|\Omega_{\mu\nu;\{n\}}\rangle = \Omega_{\mu\nu;\{n\}}\langle\alpha\beta;\{m\}|\Omega_{\mu\nu;\{n\}}\rangle, \tag{7}$$

where $\hat{L}_\mathrm{F}$ is the *time-independent* many-mode Floquet–Liouville superoperator defined in terms of the generalized tetradic-Floquet basis $|\alpha\beta;\{m\}\rangle \equiv |\alpha\rangle\langle\beta|\otimes|\{m\}\rangle$, with $\{m\} = m_1, m_2, ...m_M$.

The structure of the Floquet–Liouville super-matrix $\hat{L}_\mathrm{F}$ is illustrated in fig. 1 for the two-level two-mode case. The super-eigenvalues and eigenvectors of $\hat{L}_\mathrm{F}$ possess the following important properties: (i) $\mathrm{Im}(\Omega_{\mu\nu;\{n\}}) < 0$, (ii) $\Omega_{\mu\nu;\{n+k\}} = \Omega_{\mu\nu;\{n\}} + \Sigma_{i=1}^M k_i\omega_i$, and (iii) $\langle\alpha\beta;\{m+k\}|\Omega_{\mu\nu;\{n+k\}}\rangle = \langle\alpha\beta;\{m\}|\Omega_{\mu\nu;\{n\}}\rangle$. Further, it can be shown that in the limit of $\gamma_{\alpha\beta} = \Gamma_{\alpha\beta} = 0$ (i.e. no relaxations), the super-eigenvalues Ω and eigenvectors $|\Omega\rangle$ of $\hat{L}_\mathrm{F}$

$$\hat{L}_F = \begin{bmatrix} A+2\omega_2 I & B & 0 & 0 & 0 \\ B^* & A+\omega_2 I & B & 0 & 0 \\ 0 & B^* & A & B & 0 \\ 0 & 0 & B^* & A-\omega_2 I & B \\ 0 & 0 & 0 & B^* & A-2\omega_2 I \end{bmatrix}$$

WHERE

$$A = \begin{bmatrix} C+2\omega_1 I & X & 0 & 0 & 0 \\ X^* & C+\omega_1 I & X & 0 & 0 \\ 0 & X^* & C & X & 0 \\ 0 & 0 & X^* & C-\omega_1 I & X \\ 0 & 0 & 0 & X^* & C-2\omega_1 I \end{bmatrix}$$

$$B = \begin{bmatrix} Y & 0 & 0 & 0 & 0 \\ 0 & Y & 0 & 0 & 0 \\ 0 & 0 & Y & 0 & 0 \\ 0 & 0 & 0 & Y & 0 \\ 0 & 0 & 0 & 0 & Y \end{bmatrix} \quad C = \begin{bmatrix} -i(\gamma_{ab}+\gamma_{ba}) & 0 & 0 & 0 \\ i\gamma_{ab} & -i\gamma_{ba} & 0 & 0 \\ 0 & 0 & -\omega_{ba}-i\Gamma_{ba} & 0 \\ 0 & 0 & 0 & \omega_{ba}-i\Gamma_{ba} \end{bmatrix}$$

AND

$$X = \begin{bmatrix} 0 & 0 & -V_{ba}^{(1)} & V_{ab}^{(1)} \\ 0 & 0 & V_{ba}^{(1)} & -V_{ab}^{(1)} \\ -V_{ab}^{(1)} & V_{ab}^{(1)} & 0 & 0 \\ V_{ba}^{(1)} & -V_{ba}^{(1)} & 0 & 0 \end{bmatrix} \quad Y = \begin{bmatrix} 0 & 0 & -V_{ba}^{(2)} & V_{ab}^{(2)} \\ 0 & 0 & V_{ba}^{(2)} & -V_{ab}^{(2)} \\ -V_{ab}^{(2)} & V_{ab}^{(2)} & 0 & 0 \\ V_{ba}^{(2)} & -V_{ba}^{(2)} & 0 & 0 \end{bmatrix}$$

Fig. 1. Structure of the Floquet–Liouville super-matrix $\hat{L}_F$ for the case of two-level systems (with level spacing ω_{ba}) in linearly polarized bichromatic fields. ω_1 and ω_2 are the two radiation frequencies, $V_{ab}^{(i)}$ ($i = 1,2$) the electric dipole couplings, and γ_{ab}, γ_{ba}, and $\Gamma_{ba} = (\gamma_{ab} + \gamma_{ba})/2$ are relaxation parameters.

are related to the quasi-energy eigenvalues λ and eigenvectors $|\lambda\rangle$ of $\hat{H}_F$, where $\hat{H}_F$ is the Floquet Hamiltonian for the non-damping case [5], by the following relations:

$$\Omega_{\alpha\beta;\{m\}} = \lambda_{\alpha,\{0\}} - \lambda_{\beta,\{0\}} + \sum_{i=1}^{M} m_i\omega_i, \tag{8}$$

$$\langle\mu\nu;\{k\}|\Omega_{\alpha\beta;\{0\}}\rangle = \sum_{\{n\}} \langle\mu,\{n\}|\lambda_{\alpha,\{0\}}\rangle\langle\lambda_{\beta,\{0\}}|\nu,\{n-k\}\rangle. \tag{9}$$

Thus the super-eigenvalues Ω have the physical interpretation as the "difference spectrum" of the quasi-energies.

In terms of the eigenvalues and eigenvectors of the superoperator $\hat{L}_F$, the reduced density matrix $\boldsymbol{\rho}(t)$ can be expressed as $\hat{\boldsymbol{\rho}}(t) = \hat{U}(t;t_0)\,\hat{\boldsymbol{\rho}}(t_0)$, where $\hat{U}$ is the super-evolution-operator given by, in matrix form,

$$\hat{U}_{\alpha\beta;\mu\nu}(t;t_0) = \sum_{\{m\}} \Big(\langle\alpha\beta;\{m\}|\exp[-i\hat{L}_F(t-t_0)]\,|\mu\nu;\{0\}\rangle$$
$$+\gamma_0\delta_{\mu\nu} \sum_{\sigma\tau} \sum_{\{k\}} \langle\alpha\beta;\{m\}|\Omega_{\sigma\tau;\{k\}}\rangle\langle\Omega^*_{\sigma\tau;\{k\}}|00;\{0\}\rangle\,\{1-\exp[-i\Omega_{\sigma\tau;\{k\}}(t-t_0)]\}/i\Omega_{\sigma\tau;\{k\}} \Big)$$
$$\times \exp\left(i\sum_{j=1}^{M} m_j\omega_j t\right). \tag{10}$$

Furthermore, since $\mathrm{Im}\,\Omega < 0$ for all Ω, the reduced density matrix has a simple form at large times $t\to\infty$,

$$\rho_{\alpha\beta}(t) \xrightarrow[t\to\infty]{} \gamma_0 \sum_{\{m\}} \sum_{\sigma\tau} \sum_{\{k\}} (\langle\alpha\beta;\{m\}|\Omega_{\sigma\tau;\{k\}}\rangle\langle\Omega^*_{\sigma\tau;\{k\}}|00,\{0\}\rangle/i\Omega_{\sigma\tau;\{k\}})\exp\left(i\sum_{j=1}^{M} m_j\omega_j t\right), \tag{11}$$

which is *oscillatory* rather than completely *stationary* as would be the case in the RWA limit.

To elucidate the usefulness of the current approach, we consider the first study of the *multiphoton* resonance fluorescence spectrum of an ensemble of two-level systems (a,b) of opposite parity driven by polychromatic fields in a thermal bath undergoing purely radiative relaxation. The relevant quantity is the auto-correlation function [7], of the transition dipole operators $\hat{d}^+ = |b\rangle\langle a|$ and $\hat{d} = |a\rangle\langle b|$, namely, $g(t;t') = \langle \hat{d}^+(t')\,\hat{d}(t)\rangle$, $t > t'$, in normal order. The two-time average $g(t;t')$ can be evaluated by the use of the quantum regression theorem [8] and expressed as

$$g(t;t') = \hat{U}_{\mathrm{ba;aa}}(t;t')\,\hat{\rho}_{\mathrm{ab}}(t') + \hat{U}_{\mathrm{ba;ba}}(t;t')\,\hat{\rho}_{\mathrm{bb}}(t'), \tag{12}$$

where $\hat{U}$ is given in eq. (10). The important feature here is the non-stationary nature of the correlation function $g(t;t')$ at large times t', i.e. $g(t;t')$ depends upon both the correlation time $\tau = t - t'$ and the starting time t'. (Note that in the RWA limit, $g(t;t') \to g(\tau)$, independent of t'.) A full exploration of the time-dependent physical spectrum based on the extension of the time-dependent notion of the fluorescence spectrum [9] will be discussed elsewhere [10]. Here we only present the results for the time-averaged power spectrum defined by

$$\bar{I}(\omega) = \mathrm{Re}\left(\int_0^\infty e^{i\omega\tau}\,\bar{g}(\tau)\,d\tau\right) = \bar{I}_{\mathrm{coh}} + \bar{I}_{\mathrm{inc}}, \tag{13}$$

where

$$\bar{g}(\tau) = (1/T_s)\int_0^{T_s} dt'\,g(t;t') \quad (t' \to \infty) \tag{14}$$

is the time-averaged correlation function, assuming the resolution time of the detector T_s is much larger than the characteristic time of the laser fields (i.e. $T_s \gg \max\{2\pi/\omega_i\}$). The power spectrum $\bar{I}(\omega)$ consists of the coherent part, $\bar{I}_{\mathrm{coh}}(\omega)$, and the incoherent part, $\bar{I}_{\mathrm{inc}}$. Only the incoherent (fluorescence) spectrum is given here:

$$\bar{I}_{\mathrm{inc}}(\omega) = -\gamma_{\mathrm{ba}}\,\mathrm{Re}\left(\sum_{\{m\}} (AB + CD)\right), \tag{15}$$

where

$$A = \sum_{\mu\nu}\sum_{\{k\}} \langle \mathrm{ba};\{0\}|\Omega_{\mu\nu;\{k\}}\rangle\langle\Omega^*_{\mu\nu;\{k\}}|\mathrm{ba};\{m\}\rangle\,(\Omega_{\mu\nu;\{k\}} - \omega)^{-1},$$

$$B = \sum_{\mu\nu}\sum_{\{k\}} \langle \mathrm{bb};\{m\}|\Omega_{\mu\nu;\{k\}}\rangle\langle\Omega^*_{\mu\nu;\{k\}}|\mathrm{aa};\{0\}\rangle/\Omega_{\mu\nu;\{k\}},$$

$$C = \sum_{\mu\nu}\sum_{\{k\}} \langle \mathrm{ba};\{0\}|\Omega_{\mu\nu;\{k\}}\rangle\langle\Omega^*_{\mu\nu;\{k\}}|\mathrm{aa};\{m\}\rangle\,[1 + i\gamma_{\mathrm{ba}}(\Omega_{\mu\nu;\{k-m\}})^{-1}]\,(\Omega_{\mu\nu;\{k\}} - \omega)^{-1},$$

$$D = \sum_{\mu\nu}\sum_{\{k\}} \langle \mathrm{ab};\{m\}|\Omega_{\mu\nu;\{k\}}\rangle\langle\Omega^*_{\mu\nu;\{k\}}|\mathrm{aa};\{0\}\rangle/\Omega_{\mu\nu;\{k\}}.$$

Eq. (15) shows that the incoherent scattered light contains an infinite number of frequency components at the positions defined by the denominator $[\Omega_{\mu\nu;\{k\}} - \omega]^{-1}$, where $\Sigma_{\{k\}} \equiv \Sigma_j k_j$ must be odd integers if $\mu = \nu$ and even integers if $\mu \neq \nu$. Similarly the coherently scattered light $\bar{I}_{\mathrm{coh}}(\omega)$ comprises not only the elastic components (Rayleigh scattering), but various harmonic components at $\omega = \Sigma_j m_j\omega_j$, where $\Sigma_j m_j$ must be odd integers, with

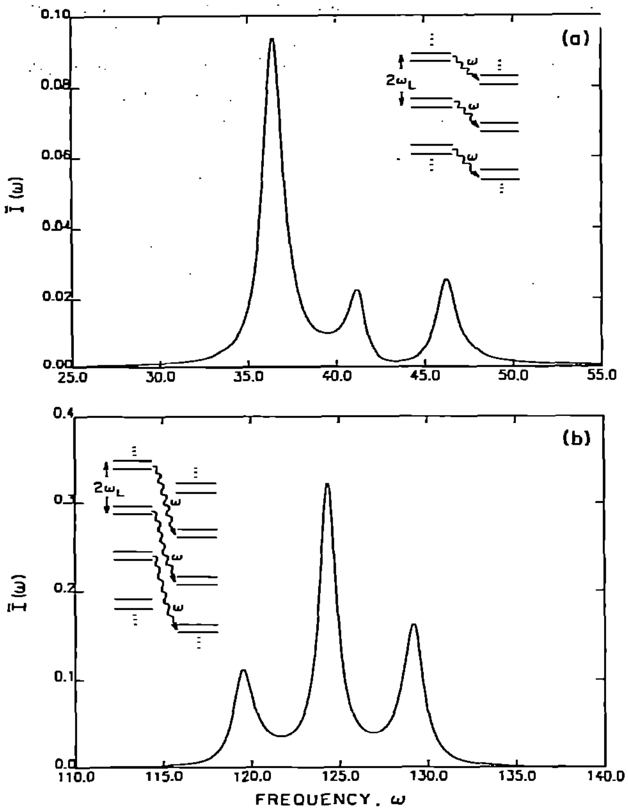

Fig. 2. Fluorescence spectra $\bar{I}(\omega)$ near (a) $\omega \approx \omega_L$, and (b) $\omega \approx 3\omega_L$, for a system of two-level atoms driven by a monochromatic field ω_L tuned at the shifted three-photon resonance. Parameters given in text. The inset in each figure shows the schematic cascade diagram (not to scale) characterizing individual fluorescence spectra, and each doublet therein represents the nearly degenerate quasi-energy levels $[(\lambda_{b,k}, \lambda_{a,k+3})$ $k = 0, \pm 1, \pm 2, ...]$ with the splitting equal to $|\Omega_{ab;0}|$.

each component infinitesimal narrow in width. It can be shown [10] that our new generalized results, eq. (15), reduce exactly to the familiar Mollow spectrum [11] in the weak field (one-mode) RWA limit.

As an illustration of new features predicted by eq. (15), we consider an ensemble of two-level atoms driven by a strong linearly polarized monochromatic field of frequency ω_L. The two levels are separated by $\omega_{ba} = E_b - E_a = 100.0$ (arbitrary units) and the spontaneous decay rate from the upper level b to the ground level a is $\gamma_{ba} = 1.0$. The Rabi frequency characterizing the interaction strength of the atom with the field is $V_{ab} = \frac{1}{2}|\langle a|\mu \cdot \varepsilon|b\rangle| = 25.0$. Figs. 2a and 2b show the induced multiphoton resonance fluorescence power spectrum $[\bar{I}_{inc}(\omega)]$ near $\omega \approx \omega_L$ and $3\omega_L$, with the laser field tuned at the (ac Stark-shifted) three-photon resonance frequency $\omega_L = 41.295$. Owing to the strong mixings of the set of unperturbed nearly degenerate three-photon resonant tetradic-Floquet states, namely, $\{|aa,0\rangle, |bb,0\rangle, |ab,3\rangle, |ba,-3\rangle\}$, the fluorescence light is most intense at $\omega \approx 3\omega_L$ (fig. 2b), though the fundamental light ($\omega \approx \omega_L$) is comparable in intensity (fig. 2a). Higher-order fluorescence lights, $\omega \approx 5\omega_L$, $7\omega_L$, etc., diminish in intensity rapidly (not shown). All fluorescence spectra shown here exhibit asymmetric three-peak structure rather than the symmetric triplet pattern in the one-photon resonant case [11] ($\omega_{ba} \approx \omega_L$). The asymmetric pattern about the central component of the three peaks at $\omega \approx \omega_L$ and $3\omega_L$ can be attributed to the significant field mixings of the three-photon resonant tetradic-Floquet states shown above with other non-resonant bases such as $|ab;1\rangle$ and $|ba;-1\rangle$. As a general rule, when the laser field is intense enough to induce multiphoton resonances (say $\omega_{ba} \approx (2n+1)\omega_L$), the dominant fluorescence component always occurs at $\omega \approx (2n+1)\omega_L$. Components in the lower-frequency side of the predominant one can have comparable intensities and often exhibit large asymmetry in the three-peak structures, while components in the higher-frequency side usually decrease rapidly in intensity as the harmonic order increases.

In summary, we have shown that the many-mode Floquet theory [5] can be extended to treat the time-dependent Liouville equation, and that the resulting generalization provides a powerful time-independent non-perturbative technique for the treatment of intense field multiphoton processes (undergoing relaxations) in polychromatic fields, much beyond the conventional RWA limit. Extension of the method to the study of Raman scattering, collisional redistribution of radiation, and renormalized non-linear susceptibility, etc., is in progress.

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